CHEMICAL CONVERSION OF ZINC OXIDE - ORGANIC RESIN FILMS TO HYDROPHILIC SURFACES

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The paper describes a chemical method of rendering water-receptive the surfaces of thin, coherent, adherent, paint-like coatings containing zinc oxide and an organic resin binder. The surfaces of the coatings initially are very hydrophobic, but for certain uses are required to be made hydrophilic and to retain their water-receptive properties for an extended period of time (Kurz, 1960, 1961).

The chemical process presented here is based upon knowledge that certain water-insoluble metallic ferrocyanides and ferricyanides exhibit and retain excellent hydrophilic properties. Zince ferrocyanide and zinc ferricyanide are among these. Accordingly, using suitable conditions of chemical treatment it was found possible to make water-receptive the zinc oxide portions of hydrophobic coatings. The conversion of the surfaces of these coatings from a hydrophobic to a hydrophilic state apparently involves forming on the surface of the zinc oxide aggregates adherent deposits of insoluble zinc ferro- or ferricyanide according to the ferrocyangen compound used in the treatment reaction.

It is believed that these ferro- and ferricyanides are hydrophilic because they are hydrated or hydratable, e.g., $Zn_2Fe(CN)_6 \cdot 5H_2O$, $Zn_3K_2[Fe(CN)_6]_2 \cdot 28H_2O$, $Zn_3Na_2[Fe(CN)_6]_2 \cdot 4H_2O$, $Zn_3H_2[Fe(CN)_6]_2 \cdot 11H_2O$, $Zn_3[Fe(CN)_6]_2 \cdot 13H_2O$, $Zn_{16}K[Fe(CN)_6]_{11} \cdot 33H_2O$. Thus, it appears plausible that the molecules of water of hydration incorporated in an insoluble zinc ferro- or ferricyanide on the surface of the treated coating can associate readily by hydrogen bonding with water from an external source, thereby endowing hydrophilic properties to the surface.

CHEMISTRY OF THE PROCESS

To produce a surface deposit of an insoluble zinc-containing ferrocyanide on zinc oxide aggregates dispersed in a resin binder it is necessary to ionize partially or totally the zinc atoms on the surface. Zinc oxide is quite insoluble in water. Consequently direct metathesis with ferrocyanide or ferricyanide ions in neutral aqueous solution would be very slow at best and would depend on the relative solubilities of the oxide and the complex zinc cyanide. It was found that no measurable reaction occurs in ten minutes between a neutral ferro- or ferricyanide solution and an initially hydrophobic coating containing zinc oxide. However, zinc oxide is readily soluble in dilute mineral or organic acids. Accordingly zinc ions may be produced as follows by acids:

$$ZnO + H^+ \rightarrow (ZnOH)^+ \quad (1)$$

$$(ZnOH)^+ + H^+ \rightarrow Zn^{++} + H_2O. \quad (2)$$

The ferrocyanide or ferricyanide deposits formed on zinc oxide dispersed in a resin binder apparently are quite adherent (they resist prolonged rinsing with water and also repeated exposure to dilute acid solutions). Therefore, it is possible that the reaction between the oxide aggregate and dilute acid may produce in many instances a partially ionized zinc atom which is still bonded to the aggregate, for example:

$$\begin{array}{l} -Zn \\ \quad >O \\ -Zn \\ \\ -Zn \\ \quad >O \\ -Zn \end{array} \quad + 4H^+ \rightarrow \quad \begin{array}{l} -Zn^+ \\ \\ -Zn^+ \\ \\ -Zn^+ \\ \\ -Zn^+ \end{array} \quad + 2H_2O. \quad (3)$$

Aggregate — Ionized Aggregate

Zinc ions formed by the action of acid as shown above are free to react with ferro- or ferricyanide ions as follows, for example:

$$3Zn^{++} + 2NaFe(CN)_6^{\equiv} \rightarrow Zn_3Na_2[Fe(CN)_6]_2 \quad (4)$$

$$\begin{matrix} -Zn^+ \\ -Zn^+ \\ -Zn^+ \end{matrix} + NaFe(CN)_6^{\equiv} \rightarrow \begin{matrix} -Zn \\ -Zn-[NaFe(CN)_6]. \\ -Zn \end{matrix} \quad (5)$$

Equations 4 and 5 are written as shown because when nonalkali metallic cations react with an excess of alkali-metal ferrocyanide (or ferricyanide) the precipitate is invariably a mixed product (Williams, 1949; American Cyanamid Company, 1953). This may be either a double salt such as, for example, $3Zn_2Fe(CN)_6 \cdot Na_4Fe(CN)_6$, or a mixed salt such as $Zn_3Na_2]Fe(CN)_6|_2$ (or analogous ferricyanides when $Fe(CN)_6^{\equiv}$ is used in place of $Fe(CN)_6^{\equiv}$ as the reacting anion). Further argument in favor of the mixed zinc-alkali metal product is that the double ferrocyanides of zinc with potassium and ammonium ions are said to be less soluble in water than is zinc ferrocyanide (American Cyanamid Company, 1953).

TABLE 1

Treatment solutions used to render coatings containing zinc oxide water-receptive

Salt used	Concentration Wt. per cent	Acid used	Concentration per cent Weight	Concentration per cent Volume	Immersion Time	Coating water receptive
Sodium Ferrocyanide*	10	Acetic Acid	—	2	1 min.	yes
" "	5	" "	—	2	1 min	yes
" "	5	" "	—	2	45 sec	yes
" "	5	" "	—	2	30 sec	yes
" "	5	" "	—	2	15 sec	yes
" "	4	" "	—	2	1 min	yes
" "	2	" "	—	2	1 min	yes
" "	2	" "	—	1	1 min	yes
" "	2	" "	—	0.5	1 min	yes
" "	1	" "	—	2	1 min	yes
" "	0.5	" "	—	2	1 min	yes
" "	0.25	" "	—	2	1 min	yes
" "	5	None	—	—	10 min	no
" "	2.5	Oxalic Acid	2.5	—	1 min	yes
" "	2.5	" "	2.5	—	30 sec	yes
" "	2	" "	1	—	2 min	yes
" "	2	Tartaric Acid	1	—	3 min	yes
" "	2	Citric Acid	1	—	3 min	yes
" "	2	Hydrochloric Acid	—	2	1 min	yes
Potassium Ferrocyanide*	5	None	—	—	1 min	no
" "	5	Acetic Acid	—	2	1 min	yes
Calcium Ferrocyanide*	5	None	—	—	1 min	no
" "	5	Acetic Acid	—	2	1 min	yes
Potassium Ferricyanide*	5	None	—	—	2 min	no
" "	5	Acetic Acid	—	2	1 min	yes
" "	5	" "	—	1.6	1 min	yes
" "	5	" "	—	0.8	1 min	yes
" "	5	" "	—	0.4	1 min	yes
" "	5	" "	—	0.2	1 min	yes

*Sodium Ferrocyanide—$Na_4Fe(CN)_6 \cdot 10H_2O$ Potassium Ferrocyanide—$K_4Fe(CN)_6 \cdot 3H_2O$
Calcium Ferrocyanide—$Ca_2Fe(CN)_6 \cdot 12H_2O$ Potassium Ferricyanide—$K_3Fe(CN)_6$

EXPERIMENTAL PROCEDURE AND RESULTS

Table 1 shows a summary of treatment conditions which have been used in experiments concerned with making hydrophobic coatings containing zinc oxide readily wettable by water. Specimen swatches of the coating on suitable supporting substrates (usually metal) were immersed in the treatment solutions for the times specified, then tested for water receptivity. This was done by holding the treated specimen in a stream of water, then removing the specimen and observing the continuity and persistence of the film of water. When dried, the treated coatings could be rewetted easily and sustained a continuous film of water over the treated portion of the specimen. The untreated portion of the coating remained as hydrophobic as it was when originally formed. The treated coating could be dried and rewetted repeatedly and could be rinsed in water for hours without losing its hydrophilic properties.

REFERENCES

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